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Environmentally Friendly Method for the Separation of Cellulose from Steam-Exploded Rice Straw and Its High-Value Applications

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Abstract

Separation of cellulose from agricultural straw is one of the key bottlenecks hindering the application of such kind of biomass resources. In this chapter, we provide three environmental-friendly ways for separation of cellulose from agricultural straw pretreated with steam explosion, which include delignification with recyclable water-polar aprotic organic solvent, selective bio-degradation of the lignin component, and extraction of cellulose with imidazolium-based ionic liquids from the steam-exploded rice straw. The isolated rice straw celluloses have been adopted as an enhancement for all-cellulose composites (ACCs) and cellulose/cement composites. Ultra-high tensile strength (650.2 MPa) can be achieved for the ACCs containing the activated straw cellulose fiber (A-SCF). The cellulose/cement composites show a significant promotion in the flexural strength and fracture toughness. The new nonderivative solvent for cellulose, tetrabutylammonium hydroxide (TBAH) aqueous solution with urea as additives has been proved to be manipulable for dissolving cellulose.

Keywords: rice straw, steam explosion, cellulose, ionic liquids, all-cellulose composites, cellulose/cement composites, cellulose solvent

1. Introduction

Due to the ever-growing demand for energy, environmental impact caused by pollution, and the depletion of fossil fuel reserves, the demand for materials from renewable resources has

become an important matter [1, 2]. Lignocellulose biomass is considered one of replacing chemicals as well as fuels based on oil [3]. Agricultural residues is one of the most valuable and renewable lignocellulosic biomass as well as a promising alternative for cellulosic materials. Among different sources of agricultural residues, rice straw has been extensively investigated because it is one of the most consumed cereals in the world, about 650–975 million tons per year all over the world [4, 5]. Rice straw is composed of approximately 35% cellulose, 18% hemicellulose, and 15% lignin [6]. It can be used as raw material for conversion to high value-added products through chemical, biochemical and physical processes. However, cellulose is usually accompanied by other structural biopolymers, saying hemicellulose, and lignin. Therefore, determination of methods for the efficient separation of the constitutive biomass components has long been the major obstacles to its utilization.

Thus, novel environmental-friendly processes have been developed continuously, which include steam explosion [7], organosolv processing [8], the chlorine-free method [5], biological treatment [9], and ionic liquid isolation [10]. In this chapter, a brief review on the separation of rice straw cellulose in sustainable ways and the related utilization of the cellulose enhanced composites are systematically presented.

2. Steam explosion as pretreatment of rice straw

2.1. Introduction

Steam explosion (SE) has been a well-known technology for the pretreatment of straws during the separation of cellulose [11–13]. The critical process is the high-temperature hydrothermal treatment followed by a sudden exposure to atmospheric pressure [14].

During processing, the major hemicelluloses are partially hydrolyzed (autohydrolysis) due to high temperature transforming the acetyl groups connected with hemicellulose into acetic acid. Part of lignin can be depolymerized and leaving on the cellulose [15]. It is reported that the hydrolysis of hemicellulose separation was related to the reaction time and the pressure in the reactor [16]. For example, with the optimum condition (215°C, 7.5 min), a high-yield of sugar (81%) and ethanol (12.4%) can be obtained [17]. Therefore, the critical issue is a suitable condition of parameters, such as cooking time and the pressure, for efficient removal of hemicelluloses during the steam explosion which has been optimized by Zhou et al. [18] with a regression method in statistics.

2.2. Optimizing of conditions for steam explosion

Naturally dried rice straw was cut into pieces of about 2–3 cm in length and then shredded in a high-speed pulverizing mill. The crushing process was necessary for the effective infiltration of steam into the cell. The rice straw was then put into the reactor with a solid to liquid ratio of 3:1 (w/w). The high-temperature steam was poured in by opening a valve and cooked for a specified time, followed by explosion procedure.

Figure 1. Spatial distribution of these two factors.

Normalized	Pressure X_1 (MPa)	Cooking time X_2 (min)
1.414	3.2	32
1.000	3.0	30
0.000	2.5	25
-1.000	2.0	20
-1.414	1.8	18

Table 1. Parameter table.

A series of experiments were designed to investigate the effects of pressure X_1 (corresponding to temperature) and cooking time X_2 on the final product of hemicelluloses (γ -Cellulose) and cellulose (α -Cellulose) in the process of steam explosion by using a regression method in statistics. The number of the experiments (N) meets the equation below:

$$N = 2^m + 2m + 3 \quad (1)$$

where, m is the number of independent factors and “3” is the number of experiments in the central point, which could improve the accuracy of the regression.

The spatial distribution of these two factors (X_1 , X_2) in this regression design is illustrated in **Figure 1**. According to the earlier works of exploratory, the interval factors have been determined, as shown in **Table 1**.

The details of the experimental plan as well as the content of hemicelluloses and cellulose of the steam-exploded straw are shown in **Table 2**. The sample 11 of steam explosion in **Table 2** is selected for the comparison of the main components with the original rice straw. It is clear that most of the hemicelluloses can be hydrolyzed and extracted at the proper set of conditions for the steam explosion.

No.	X1	X2	Treatment severity $\lg R_o^a$	γ -C (%) ^b	α -C (%) ^b	DP ^c
Rice straw	—	—	—	17.98	35.06	1123
1	1.000	1.000	6.19	3.01	70.43	229.5
2	-1.000	1.000	5.60	8.66	69.85	303.3
3	1.000	-1.000	6.01	3.84	65.03	198.4
4	-1.000	-1.000	5.42	3.25	67.58	272.7
5	0	1.414	5.92	6.29	72.96	360.2
6	0	-1.414	5.67	6.68	70.51	276.2
7	1.414	0	6.25	2.72	61.77	246.0
8	-1.414	0	5.37	8.46	70.49	418.6
9	0	0	5.81	1.45	64.80	268.3
10	0	0	5.81	1.38	64.72	266.0
11	0	0	5.81	1.10	64.65	270.9

^aRefers to the strength of the steam explosion and could be calculated by Eq. (2).

^bThe contents of α -Cellulose and γ -Cellulose, respectively, which are determined according to Tappi method T203 cm-99.

^cThe intrinsic viscosity of α -Cellulose ($[\eta]$) that is measured in cupriethylenediamine (CED) solution, and from which the DP (degrees of polymerization) could be calculated by the equation below, according to SCAN-CM 15:88 standard.

Table 2. Effect of reaction time and pressure on the final content of hemicelluloses and cellulose [18].

The value of $\lg R_o$ is proportional to the strength of steam explosion. Additional hydrolysis of α -Cellulose may happen along with higher $\lg R_o$, as indicated by sample 7 in **Table 2**.

$$R_o = \int_0^{t_{min}} \exp\left(\frac{T[^\circ C] - 100}{14.75}\right) \cdot dt \tag{2}$$

$$DP^{0.76} = [\eta]/2.28 \tag{3}$$

Experimental data in **Table 2** have been fitted to the following second-order polynomial:

$$Y_i = a + bX_1 + cX_2 + dX_1^2 + eX_2^2 + fX_1 X_2 \tag{4}$$

where Y_i refers to α -Cellulose, γ -Cellulose and SCAN viscosity, respectively. The symbols of a , b , c , d , e and f are the corresponding estimated parameters. Regression has been carried out using a nonlinear method with the SPSS software, and the result data are as shown in **Table 3**. R^2 values of α -Cellulose and γ -Cellulose are close to 0.9, which indicate good models for these factors. However, the model of SCAN viscosity is not well fitted, as indicated by the low value of the R^2 .

Since the regression has established good models (Eqs. 5 and 6) describing the relationships between independent factors (referring to X_1 pressure and X_2 cooking time of the steam explosion process) and the responses (referring to Y_i , final content of γ -Cellulose and α -Cellulose).

Symbols	γ -Cellulose (%)	α -Cellulose (%)	SCAN viscosity
<i>a</i>	1.31	64.72	268.42
<i>b</i>	-1.65	-1.79	-48.76
<i>c</i>	0.50	1.34	26.80
<i>d</i>	1.80	0.54	14.93
<i>e</i>	2.25	3.28	4.85
<i>f</i>	-1.56	0.78	6.95
R^2	0.896	0.861	0.332

Table 3. Characteristic constants and R^2 of the regression [18].

These relationships can be visualized, as shown in **Figure 2**. The values of coordinates of their nadirs are given in **Table 5**.

$$Y_{\gamma-C} = 1.31 - 1.65 \times X_1 + 0.50 \times X_2 + 1.80 \times X_1^2 + 2.25 \times X_2^2 - 1.56 \times X_1 \times X_2 \quad (5)$$

$$Y_{\alpha-C} = 64.72 - 1.79 \times X_1 + 1.34 \times X_2 + 0.54 \times X_1^2 + 3.28 \times X_2^2 + 0.78 \times X_1 \times X_2 \quad (6)$$

As discussed earlier, the aims of the steam explosion maximizing the removal of the γ -Cellulose and the loss of α -Cellulose. From the observation, there is no serious contradiction between these two aims, since the nadir of γ -Cellulose and α -Cellulose locates at the center and the edge, respectively. Therefore, the optimal condition for the steam explosion is 2.74 MPa and 25.3 min, according to the data in **Table 4**. Under the optimal condition, the structure of steam-exploded rice straw showed the characteristics of soft, loose and porous with different sizes distributed though all of the fiber (as shown in **Figure 3a**), which supported further separation of cellulose and lignin. The most of hemicelluloses could be efficiently hydrolyzed,

Figure 2. A 3D graphic of dependent factor (referring to final content of γ -cellulose Y_{γ}) vs. independent factors (referring to pressure X_1 and reaction time X_2 of the steam explosion process), (a) according to Eq. (5), and (b) according to Eq. (6).

	γ -Cellulose		α -Cellulose	
	Scaled factor	Factor	Scaled factor	Factor
Pressure X_1 (MPa)	0.481	2.74	1.414	3.20
Reaction time X_2 (min)	0.056	25.3	-0.374	23.1
Content of cellulose Y_i (%)	0.93		62.82	

Table 4. Factor values for the minimum of the content of γ -cellulose and α -cellulose.

Figure 3. (a) SEM images and (b) FT-IR spectra of rice straw (RS) and steam-exploded rice straw (SERS) [18].

leaving only 1% residual hemicelluloses. However, the majority of cellulose, as well as the fragmentized lignin, were retained in the size, which could be identified by the SEM observations (**Figure 3a**) and the FTIR spectra (**Figure 3b**) [18].

3. Posttreatment of steam-exploded rice straw

3.1. Selective dissolution of cellulose using ionic liquids

Ionic liquids (ILs) are emerging as promising solvents for treatment of lignocelluloses [19–23], due to its low vapor pressures. These solvents are made up of large organic cations and small

inorganic anions, which have the following key properties: (a) they are liquids below 100°C or even at room temperature; (b) high thermal stability; and (c) high polarity [24]. These properties allow to be easily adjusted to dissolve diversity of lignocellulosic biomass [25–27]. Since several kinds of ionic liquids have been found to be non-derivatized solvents for cellulose, they have been applied in such research fields as capturing the portrait of single cellulose molecule [25], and chemical modification of cellulose [19]. In this section, ionic liquids are used in separation of cellulose from steam-exploded rice straw. It is proved to be an efficient and environmentally friendly way to selectively dissolve and then recover cellulose [6].

Four kinds of ionic liquids: 1-butyl-3-methylimidazolium chloride (BMIMCl), 1-allyl-3-methylimidazolium chloride (AMIMCl), 1-benzyl-3-methyl-imidazolium chloride (BnMIMCl) and 1-benzyl-3-methyl-imidazolium trifluoroacetate (BnMIMTFA) have been synthesized according to literature [20]. Their solubility for cellulose and lignin are shown in **Table 5**. The results indicate that BnMIMCl and BnMIMTFA are efficient for dissolving lignin. BMIMCl and AMIMCl are efficient for dissolving cellulose.

AMIMCl is selected as a selective solvent to separate cellulose from the steam-exploded rice straw. The contents of acid-insoluble lignin and celluloses of the steam-exploded rice straw are 14.76 and 64.80% respectively. After dissolving in AMIMCl, there is only 0.90% acid insoluble lignin contained in the recovered cellulose. With a procedure of bleaching by immersing the separated cellulose into hydrogen peroxide aqueous solution together with ozone blowing (about 3.4 g/h produced by SZH5 ozone apparatus, Peking) was needed for bleaching. The bleached cellulose was finally obtained with a yield of 30.73%. The component analysis according to TAPPI standard methods (T 222 om-06 and T 203 cm-09) indicated no detectable acid-insoluble lignin and only 0.85% of hemicelluloses left in the final cellulose. The average degree of polymerization (DP) was 484.

The SEM image and XRD profile of the bleached cellulose are shown in **Figure 4**. As seen in **Figure 4a**, cellulose fibers could be observed clearly with average lengths more than 100 µm. The prominent peak at 22.13° denotes the (002) reflection (as shown in **Figure 4b**). However, the characteristic (101) and (101) peaks (2θ between 15 and 17°) are not as distinct as those in cotton [24], but combine into one broad peak at 15.728°.

The FTIR spectra of the original rice straw, steam-exploded rice straw as well as the bleached cellulose had been provided, **Figure 5a**. The peaks at 1510, 1465 and 1423 cm⁻¹ in the sample RS, corresponded to the skeleton stretch of the benzene ring, mainly contributed by lignin. These peaks reduced in steam-exploded sample and disappeared in the bleached cellulose, indicating that the lignin could be removed by selective dissolving of IL. The ¹³C CP/MAS solid-state NMR spectrum of the bleached cellulose shown in **Figure 5b** suggests that highly purified cellulose is obtained. The chemical shifts at 62 and 64 ppm are assigned to C6 of the primary alcohol group

Ionic liquid	AMIMCl (%)	BMIMCl (%)	BnMIMTFA (%)	BnMIMCl (%)
Cellulose	5.2	4.9	-	-
Lignin	-	-	4.9	3.9

“-” represents nearly no sample can be dissolved.

Table 5. Solubility of the four ILs for cellulose and lignin [6].

Figure 4. (a) SEM image and (b) XRD profile of bleached cellulose [6].

of cellulose, 71 and 74 ppm attributed to C2, C3 and C5, the ring carbons of cellulose. The peaks at 83 and 88 ppm associated with C4, and 104 ppm associated with C1. The feeble signals at 173 and 20 ppm attributed to the carbonyl and the methyl resonances, respectively.

3.2. Organosolve dissolution of lignin from the steam-exploded straw size

The organosolv process can effectively degrade lignin, which is mainly used osmosis to break and decompose the internal chemical bonds of cellulose and hemicellulose [28–30]. It is considered to be an environmentally friendly way because it can be recycled conveniently, which demonstrates its potential utilization in isolation of lignocellulosic biomass [8]. Moreover, the structure of the dissolved component will be protected from degrading under such moderate conditions, which is benefit for further utilization. The efficient solvent for delignification combined with steam explosion treatment has been realized as the separation of the three components that are cellulose, hemicellulose and lignin. However, few organosolv process

Figure 5. (a) FT-IR spectra and (b) ¹³C CP/MAS solid-state NMR spectrum of rice straw (RS); steam-exploded rice straw (SERS); bleached cellulose (BC) [6].

have been proved attractive as regards efficiency and selectivity, even though intensive researches have been done [31, 32]. In this section, consideration has given on the effect of delignification with mixed solvent from steam-exploded rice straw under ambient pressure [18].

First, the rice straw is pretreated by steam explosion as the optimal conditions mentioned above. The steam-exploded rice straw was then washed with hot water (1:20 g/mL). After that, the residue was delignified by different mixed solvent to obtain crude cellulose. Finally, it was bleached with aqueous solution (1:30 g/mL, pH 11, 55°C) of 2% hydrogen peroxide and 0.2% TAED (tetraacetylenediamine) for 5 h.

The mixed solvent system and its results were summarized in **Table 6**. Comparing the delignification efficiency of H₂O-Dimethyl Sulfoxide (DMSO) (sample 7, 63.27%), H₂O-*N*-methylpyrrolidone (NMP) (sample 8, 75.14%) and H₂O-*N,N*-dimethylformamide (DMF) (sample 9, 84.78%) solvent systems to H₂O-methanol (sample 1, 57.13%), one could conclude that water-aprotic solvent system was better than water-protic solvent system for delignification. The delignification efficiency of H₂O-methanol could be further improved to 79.99% with aniline additive as the catalyst (sample 6). Similarly, aniline additive as a catalyst in the H₂O-DMF solvent system resulting in the efficiency improvement of delignification from 84.78 (sample 9) to 95.04% (sample 10).

Conclusively, the H₂O-DMF-aniline solvent system (in a volume ratio of 20:10:1) demonstrated to be the most efficient solvent for removing lignin from the steam-exploded rice straw because the DMF and aniline included amino groups might improve the dissolution of lignin.

The FTIR spectrum of the original rice straw, the steam-exploded rice straw, the delignified sample with H₂O-DMF-aniline and bleached cellulose shown **Figure 6a** indicated that the

No.	Solvent system ^a	Additives	Lignin residue (wt%)	Delignification ^b (%)
1	H ₂ O-methanol	—	7.52	57.13
2	H ₂ O-methanol	Formic acid	5.09	70.98
3	H ₂ O-methanol	Terephthalic acid	5.10	73.93
4	H ₂ O-methanol	Salicylic acid	2.89	77.33
5	H ₂ O-methanol	Sodium hydroxide	3.92	69.25
6	H ₂ O-methanol	Aniline	3.51	79.99
7	H ₂ O-DMSO	—	6.45	63.27
8	H ₂ O-NMP	—	4.36	75.14
9	H ₂ O-DMF	—	2.67	84.78
10	H ₂ O-DMF	Aniline	0.87	95.04

^aRepresents the residual cellulose-enriched fractions obtained with water, organic solvent and additives in ratios of 20:10:1 (v: v: v).

^bThe acid-insoluble lignin content in the steam-exploded rice straw is measured to be 12.75%.

Table 6. Influence of the composition of mixed solvent on the delignification process [18].

Figure 6. (a) FTIR spectra and (b) ¹³C-NMR spectra of different samples (0, original rice straw); steam-exploded rice straw (1, SERS); H₂O-DMF-aniline delignified rice straw (2, DERS); bleached cellulose (3, BC) [18].

lignin in straw could be removed and obtained pure cellulose because the absorptions at 1511 and 1429 cm⁻¹ assigned to the aromatic C=C stretch from aromatic ring in lignin became weak after the steam explosion (spectrum SERS) and delignification (spectrum DERS), and finally disappeared in the bleached cellulose (spectrum BC) [18].

Figure 6b indicated the ¹³C CP/MAS solid-state NMR spectra of the steam-exploded rice straw (SERS), delignified rice straw (DERS) and bleached cellulose (BC). All of these spectra were dominated by the resonances attributable to cellulose. Notably, two small peaks at 99.5 and 58.2 ppm in the spectrum of steam-exploded rice straw (pattern SERS) were assigned to lignin and they nearly disappear in spectrum DERS, BC, which were the delignified cellulose with the water-DMF-aniline solvent system and bleached cellulose, respectively.

3.3. Biological removal of lignin from the steam-exploded straw size

Biological treatments employ microorganisms and their enzyme systems to break down the lignin present in lignocellulosic biomass. This approach has recently attracted increased attention because of its mild condition, low energy consumption, and the absence of pollution [33, 34]. Among the microorganisms those are capable of degrading lignocelluloses, white rot fungi has a higher selectivity toward lignin with lower energy input, as well as being environmentally friendly [35].

One white rot fungus, *Phanerochaete chrysosporium* (*P. chrysosporium*), harbors at least 10 lignin peroxidases (LiP), five manganese peroxidases (MnP), and several copper oxidases in its lignin-degrading system [36, 37]. Combinatorial treatment of steam explosion and biological treatment has been considered as an effective method of separating components for various kinds of biomass. Chen et al. [38] reported the effects of the solid-state fermentation (SSF) conditions on biodegradation of steam-exploded wheat straw with *P. chrysosporium*. Under the optimum conditions of SSF, the degradation amount of lignin reached 60% on the 5th day. Zhang et al. [39] indicated that steam explosion is an important pretreatment method for biodegradation of lignin in rice straw. After steaming under 2.5 MPa for 25 min, then completely decompressed within 3 min, the steam-exploded straw was collected and dried for biodegradation treatment. In their study, the degradation rate of lignin was 31.23% without steam explosion, and 55.40%

lignin loss rate had been found on day 30 after steam explosion pretreatment. A two-stage process proposed by Zhou et al. [40] was based on the pretreatment of steam explosion and followed by a *P. chrysosporium* post-treatment for the isolation of cellulose.

As the above processes, the orthogonal experiments (using $L_{16}(4)^5$ orthogonal table) were designed (Table 8) to investigate the relationship between the delignification in SERS and the five factors. Each factor had been set based on the pretest results and a literature review (Table 7). Curves of the factors vs. the delignification was shown in Figure 7.

According to Table 8, the maximum lignin loss rate, 64.25%, was obtained with the conditions of 1% spore suspension, 70% moisture content, 0.1% T-80, initial pH of 5.0, and 28 days of fermentation. The experimental outcomes could not be used as the best SSF conditions, so the orthogonal analysis should be performed. Table 8 shows the results of orthogonal analysis for five factors used in the fermentation process and the order of importance of these factors on lignin removal was $E > C > B > D > A$. Based on the k value of the testing factors, the optimum process for fermentation is $A_3B_3C_2D_3E_4$, corresponding to 1.5% spore suspension, 0.3% T-80, 70% moisture, initial pH of 5.0, and 28 days of SSF.

According to the analysis presented above, the most important factor for delignification was SSF time. However, there was no top value of SSF time vs. delignification unlike the other four factors as shown in Figure 7. Hence, the effect of SSF time required further study.

Moisture was found to be significant to the delignification by *P. chrysosporium*. Water in SSF systems shows functions of transporting the nutrients and metabolites, which can contribute to the stability of the cellular and molecular structures. As displayed in Figure 7, until the moisture levels (70 and 75%), the delignification increased with increase of moisture. However, the delignification decreased after moisture exceeded 75% because the high moisture hampered the diffusion of oxygen into the liquid and solid phases thus limited aerobic SSF.

Figure 8 shows the effect of SSF time on the removal of lignin. The experimental results satisfactorily fitted the Boltzmann model with the decisive coefficient $R^2 = 0.9983$. The lignin content of the steam-exploded rice straw was efficiently degraded after a prolonged period. Nearly half of the highest lignin removal rate was obtained on the 7th day of fermentation. When the treatment time of using *P. chrysosporium* was 10 days, the lignin removal increased to 50.13%. Thereafter, the lignin removal rate decreased and tends to stabilize after 12 days.

Although the lignin degradation of steam-exploded rice straw is very important, too much weight loss is unexpected. The relationship between the SSF time and weight loss is shown

No.	Factor	Level 1	Level 2	Level 3	Level 4
A	Spore suspensions concentration (%)	0.5	1.0	1.5	2.0
B	T-80 concentration (%)	0.1	0.2	0.3	0.4
C	Moisture content (%)	65	70	75	80
D	Initial pH	3	4	5	6
E	SSF time (day (d))	7	14	21	28

Table 7. Factors levels for the orthogonal experiments [40].

Test no.	Factors					Delignification (%)
	A	B	C	D	E	
1	0.5	0.1	65	3	7	16.63
2	0.5	0.2	70	4	14	49.68
3	0.5	0.3	75	5	21	56.37
4	0.5	0.4	80	6	28	37.92
5	1.0	0.1	70	5	28	64.25
6	1.0	0.2	65	6	21	52.78
7	1.0	0.3	80	3	14	28.75
8	1.0	0.4	75	4	7	17.02
9	1.5	0.1	75	6	14	48.43
10	1.5	0.2	80	5	7	8.65
11	1.5	0.3	65	4	28	62.65
12	1.5	0.4	70	3	21	53.46
13	2.0	0.1	80	4	21	39.15
14	2.0	0.2	75	3	28	57.97
15	2.0	0.3	70	6	7	24.06
16	2.0	0.4	65	5	14	43.06
K_1	160.60	168.46	175.81	156.81	66.36	
K_2	162.80	169.08	191.45	168.50	170.61	
K_3	173.19	171.83	179.79	173.02	201.76	
K_4	164.93	152.15	114.47	163.19	222.79	
k_1^a	40.15	42.12	43.95	39.20	16.59	
k_2^a	40.70	42.27	47.86	42.12	42.65	
k_3^a	43.30	42.96	44.95	43.25	50.44	
k_4^a	41.23	38.04	28.62	40.80	55.70	
R^b	3.15	4.92	19.24	4.05	39.11	

^a k_1, k_2, k_3 , and k_4 are the mean values of the sum of the evaluation indexes of all levels. By comparing k values, the optimal levels of the factors can be confirmed.

^bThe range of factors ($R = \text{Max}(k_i) - \text{Min}(k_j)$) indicates the function of the corresponding factor. The larger value of R means the greater impact of the level of the factor on the experimental index.

Table 8. Experimental setup together with results of *P. chrysosporium* delignification [40].

in **Figure 9**, which turned out to be a linear relationship with decisive coefficient $R^2 = 0.99843$. The weight loss of SERS is proportional to the SSF time, differing from the results shown in **Figure 8**. Weight loss of SERS might be attributed to the removal of lignin and hemicellulose over 10 days of fermentation, after which the degradation of cellulose gradually became a major factor of SSF.

Figure 7. Curves of the factors vs. delignification [40].

In comparison with the FTIR spectrum of untreated SERS (**Figure 10a**), prominent changes could be obtained in the samples degraded after different SSF timings. The increase in the intensity of peak at 1650 cm^{-1} showed higher abundance of C=O groups of lignin, demonstrating the aromatic lignin moieties altered by oxidation with lignin biodegradation. In addition, peaks at 1510 and 1431 cm^{-1} turned weakening with increasing treatment time, implying the

Figure 8. The effect of SSF time on the removal of lignin [40].

Figure 9. The effect of SSF time on the weight loss of SERS [40].

Figure 10. (a) FTIR spectra, (b) XRD patterns, and (c) morphologies of SERS before and after SSF with *P. chrysosporium*.

aromatic skeletal carbon of lignin was destroyed by *P. chrysosporium*. The peaks at 896, 1060, and 1160 cm^{-1} disappeared with increasing SSF time, showing that the structure of cellulose has been degraded after longer treatment time. Peaks observed near 23.11° (**Figure 10b**) represent diffractions of the (002) crystal plane, indicating that the crystal type of cellulose in SERS is cellulose type-I in nature (as shown in **Figure 10b**). Fermentation appeared not to change the crystal type of cellulose. With increasing SSF time, the peak height of the (002) crystal plane decreased and the peak width at half height increased compared with untreated SERS. The morphologies of the samples before and after bio treatment had been examined by SEM (**Figure 10c**) to visually demonstrate the process of delignification and cellulose degradation by *P. chrysosporium*.

4. High-value applications of cellulose isolated from straw

All-cellulose composites (AACs) have been proposed to meet the interfacial problem in the cellulose-based composites, where both the reinforcement phase and matrix are cellulose [41–43]. Zhou et al. [44] reported that ACCs, with microcrystalline cellulose (MCC) as the matrix and the straw cellulose fibers (SCFs) as the reinforcement agent exhibited an ultra-high tensile strength (650.2 MPa, **Figure 11**).

The mechanism for the high performance of alkali-treated SCF (N-SCF) and activated SCF (A-SCF) reinforced ACCs are shown in **Figure 12**. For the ACCs/N-SCF sample (**Figure 12a**), the reinforcement mechanism is possibly related to the removal of impurities and the increase of aspect ratio. For the ACCs/A-SCF sample (**Figure 12b**), the reinforcement mechanism can be possibly attributed to the fact that both A-SCF and MCC experience the same activation process. Due to successively pre-swell with solvents (water, ethanol, *N, N*-dimethylacetamide) gradually reducing polarity, the

Figure 11. (a) Typical engineering stress–strain curves of the samples, (b) the corresponding tensile properties, where, a: Regenerated MCC, b: ACCs/activated SCF (A-SCF), c: ACCs/alkali-treated (N-SCF), and d: ACCs/activated SCF [44].

Figure 12. Schematic representations showing the reinforcement mechanism of the N-SCF (a) and the A-SCF (b) in the ACCs [44].

Figure 13. Schematic illustration for the mechanism of TBAH/urea aqueous solution dissolving cellulose. These two diagrams display various interfacial resistances between the crystal surface of natural cellulose and the solvent [49].

A-SCF and MCC molecular chains in SCF and MCC could be partially dissolved and penetrated into each other, resulting in improving entanglement density of molecular chains on the fiber surface.

Besides, the isolated cellulosic fibers of about 2–16 wt% can be introduced into the cement with a slurry vacuum de-watering technique [45]. It was found that the flexural strength and fracture toughness of the optimal sample were increased by 24.3% and 45 times, respectively.

Effective solvent system for cellulose dissolution is a long-standing goal due to the abundant hydroxyl groups on the cellulose chain form a strong, three-dimensional intermolecular and intramolecular hydrogen bonding network [46, 47]. Therefore, Zhou et al. [48] developed a new aqueous solvent for cellulose based on the quaternary ammonium hydroxide (TBAH). It was found that cellulose can be efficiently dissolved in a 40 wt% TBAH aq. solution under a cooling condition. The mechanism for the dissolution is believed to be the match of amphiphilicity between the solvent and cellulose crystal. Then, Zhou et al. [49] studied the effects of urea to the dissolution of cellulose in TBAH. It was found that a hybrid hydrate of TBAH and urea formed. Urea can serve as a hydrophobic contributor, by which the amphiphilic property of the solvent system can be adjusted. With a suitable amphiphilicity, interfacial resistance between the solvent and crystal surface can be reduced so that the crystal of natural cellulose can be effectively infiltrated and subsequently dissolved by the solvent. The schematic dissolution process of the cellulose is shown in **Figure 13**.

5. Conclusions

The steam explosion process is realized as a promising pre-treatment for the separation of cellulose from natural biomasses. It can make most of the hemicellulose hydrolyze and part of the lignin degrade, which results in loose and porous structures, which could ultimately support further separation of cellulose and lignin. One kind of ionic liquids, 1-allyl-3-methylimidazolium chloride (AMIMCl), is selected for the extraction of cellulose, due to its especially selective solubility for cellulose rather than lignin. This process with ionic liquids shows advantages of efficiency, environmentally friendly, and recyclability character. Isolation of cellulose with the organic solvent system that composes of H₂O-DMF-aniline has proved that it also been considered as an environmental-friendly approach, and up to 95.04% lignin can be dissolved out from the steam-exploded rice straw, leaving quite a small amount of hemicellulose (<1%) and lignin (<0.85%). There is no obvious decrease in the degree of cellulose crystallinity during the delignification and bleaching processes. Approximately 58% lignin can be removed under selective delignification of the steam-exploded rice straw by *P. chrysosporium*. The isolated cellulose fiber from the rice straw can serve as a reinforcement material for the advanced mechanical property of composites. The prepared ACCs exhibit an ultra-high tensile strength. The cellulose/cement composites show a remarkable improvement in the flexural strength and fracture toughness. Cellulose can be efficiently dissolved in a 40 wt% TBAH aq. solution under a cooling process.

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